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54 Irradiation curable, aqueous binding agent dispersions

57 Irradiation curable, aqueous binding agent dispersions, containing the following as binding agent components  
(A) 5 to 95 weight %, relative to the total quantity of components (A), (B) and (C), of a polyurethane dispersed in water, which has a K-value greater than 40 (measured in dimethyl formamide) or which is not soluble in dimethyl formamide and which exhibits a content of polymerizable ethylenic unsaturated groups of a maximum of 0.2 moles per 100 g of polyurethane, and  
(B) 5 to 95 weight %, relative to the total quantity of components (A), (B) and (C), of a prepolymer or of a prepolymer mixture dispersed in water with a content of 0.1 to 1.0 mole of polymerizable ethylenic unsaturated groups per 100 g of prepolymer or of prepolymer mixture and with a molecular weight of 300 to 10,000, whereby the K-value (measured in dimethyl formamide) is smaller than 40, and  
(C) 0 to 30 weight %, relative to the total quantity of the components (A), (B) and (C), of a protective colloid.

## Description

The invention concerns irradiation curable, aqueous binding agent dispersions containing

(A) 5 to 95 weight %, relative to the total quantity of components (A), (B) and (C), of a polyurethane dispersed in water, which has a K-value greater than 40 (measured in dimethyl formamide) or which is not soluble in dimethyl formamide and which exhibits a content of polymerizable ethylenic unsaturated groups of a maximum of 0.2 moles per 100 g of polyurethane, and

(B) 5 to 95 weight %, relative to the total quantity of components (A), (B) and (C), of a prepolymer or of a prepolymer mixture dispersed in water with a content of 0.1 to 1.0 mole of polymerizable ethylenic unsaturated groups per 100 g of prepolymer or of prepolymer mixture and with a molecular weight of 300 to 10,000, whereby the K-value (measured in dimethyl formamide) is smaller than 40, and

(C) 0 to 30 weight %, relative to the total quantity of the components (A), (B) and (C), of a protective colloid.

Irradiation curable, aqueous binding agent dispersions of polyurethanes, polyesters, polyethers and of other prepolymers are known, for example, from the German patent DE A 28 53 921. In the German patent DE A 34 37 918, aqueous polyurethane acrylate dispersions are described in which the polyurethane acrylates exhibit a double bond number of 2.5 to 15 g of bromine per 100 g of polyurethane acrylate ( $\pm$  0.016 to 0.09 mole of bromine or mole double bonds per 100 g of polyurethane acrylate). The coatings produced with these dispersions are characterized by good elastic properties. Based on the low number of double bonds and on the associated low cross linking density, the hardness of these coatings is however not satisfactory.

The task of the current invention was therefore to produce aqueous, irradiation curable binding agent dispersions which yield coatings with very good elasticity and great hardness. At the same time, the coatings should adhere well to the substrate surfaces and exhibit a good resistance to solvents and chemicals.

Accordingly, aqueous, irradiation curable binding agent dispersions were found in accordance with claim 1.

Further embodiments concern the individual components of the binding agent dispersions as well as their application for coating surfaces.

Suitable polyurethanes (A) are obtained by reacting polyisocyanates with polyamines or with polyols as chain elongators, possibly with monofunctional alcohol compounds or amine compounds and possibly with compounds with at least one ethylenic unsaturated group and with at least one hydroxyl or amino group reacting to isocyanate.

Are used for the production of polyurethane in particular, relative to

- a) 1 gram equivalent of NCO of a polyisocyanate, the following gram equivalent quantities of compounds with one or several groups that react to isocyanate:
- b) 0.1 - 0.8 gram equivalents of OH of a polyol with a molecular weight between 400 and 6,000 g/ mole
- c) 0 - 0.8 gram equivalents of OH of a polyol with a molecular weight between 62 and 399 g/ mole
- d) 0 - 0.4 gram equivalents of NH of a polyamine with at least two amino groups that react to isocyanate
- e) 0 - 0.4 gram equivalents of OH of an amino alcohol with an amino group that reacts to isocyanate
- f) 0 - 0.5, preferably 0.05 - 0.5 gram equivalents of OH or of NH of a compound with ionic groups or with groups that are convertible into ionic groups with at least one hydroxyl group or amino group that reacts to isocyanate,
- g) 0 - 0.2 gram equivalents of OH or of NH of monofunctional amine compounds or hydroxyl compounds and possibly with
- h) as many gram equivalents of OH of a compound with at least one ethylenic unsaturated group, so that in the polyurethane, a maximum of 0.2 moles of polymerizable ethylenic unsaturated groups ( $> C = C <$  groups) are present per 100 grams of polyurethane,

whereby the sum of the gram equivalents of the amino or hydroxyl groups reacting to the isocyanate generally amounts to from 0.9 to 1.1, and in particular from 0.95 to 1.05.

Preferably, the contents of polymerizable ethylenic unsaturated groups in the polyurethane amounts to from 0.01 to 0.2, especially preferred from 0.02 to 0.08 moles per 100 grams of polyurethane.

The polyurethane has a K-value (as per Fikent, cellulose chemistry 13, 58 (1932)) measured in dimethyl formamide at 25°C of more than 40 or is insoluble in dimethyl formamide at 25°C, for example, due to its particularly high molecular weight or because it is a cross linked polyurethane, such that the K-value no longer can be determined.

Concerning the formulation components of the ethylenic unsaturated polyurethane, the following must be noted:

Suitable polyisocyanates are a) organic compounds which exhibit at least two free isocyanate groups. Preferably,  $X(NCO)_2$  diisocyanates are used, whereby X signifies an aliphatic hydrocarbon group with 4 to 12 carbon atoms, a cyclo- aliphatic hydrocarbon group with 6 to 15 hydrocarbon atoms, an aromatic hydrocarbon group with 6 to 15 hydrocarbon atoms or an aral- aliphatic hydrocarbon group with 7 to 15 carbon atoms. Examples for such diisocyanates are tetra- methylene diisocyanate, hexa- methylene diisocyanate, dodeca- methylene diisocyanate, 1,4- diisocyanato- cyclohexane, 1- isocyanato- 3,5,5- trimethyl- 5- isocyanato methyl cyclohexane, 4,4'- diisocyanato dicyclohexyl- methane, 4,4'- diisocyanato- dicyclo hexyl

propane- (2,2), 1,4- diisocyanato- benzol, 2,4- diisocyanato- toluene, 2,6- diisocyanato- toluene, 4,4'- diisocyanato- diphenyl methane, p- xylylene diisocyanate, as well as mixtures consisting of these compounds such as, in particular, mixtures of aliphatic or cycloaliphatic and aromatic diisocyanates with a molar ratio of 1 : 4 through 5 : 1. It is also possible to concurrently use in part with these the higher functional polyisocyanates that are known in polyurethane chemistry or to also use known modified polyisocyanates exhibiting for example carbodiimide groups, allophanate groups, isocyanurate groups, urethane groups and/or biuret groups.

In the case of b) polyols with a molecular weight range between 400 and 6,000 g/ mole, preferably between 800 and 4,000 g/ mole, especially preferred between 1,400 and 3,000 g/ mole, we are dealing with polyester polyols or polyether polyols.

In the case of polyester polyols we are dealing in particular with the known transformation products of polyvalent, preferably of bivalent and possibly additionally of trivalent alcohols with polyvalent, preferably bivalent carboxylic acids. In place of the free polycarboxylic acids, the corresponding polycarboxylic acid anhydrides can also be used, or the corresponding polycarboxylic acid esters of low alcohols or of mixtures thereof, for the production of polyester polyols. The polycarboxylic acids can be aliphatic, cycloaliphatic, aromatic or heterocyclic, and possibly substituted by halogen atoms for example and/or be unsaturated. Let us name as examples for these: succinic acid, adipic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, isophthalic acid, trimellitic acid, phthalic acid anhydride, tetrahydrophthalic acid anhydride, hexa- hydrophthalic acid anhydride, tetrachlorophthalic acid anhydride, endomethylene tetrahydro- phthalic acid anhydride, glutaric acid anhydride, maleic acid, maleic acid anhydride, fumaric acid, dimeric fatty acids. As polyvalent alcohols, the following come under consideration, for example, ethylene glycol, propylene glycol- (1,2) and - (1,3), butanediol- (1,4), -(1,3) and -(2,3), butenediol- (1,4), butinediol- (1,4), pentanediol- (1,5), hexanediol- (1,6), octanediol- (1,8), neopentyl glycol, cyclohexane dimethanol (1,4- bis- hydroxymethyl cyclohexane), 2- methyl- 1,3- propanediol, pentanediol- (1,5), glycerin, trimethylol propane, hexanetriol- (1,2,6), butanetriol- (1,2,4), trimethylol ethane, and furthermore diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol, dipropylene glycol, polypropylene glycol, dibutylene glycol and polybutylene glycol.

Also suitable are polyester polyols on a lactone base, whereby we are dealing with homopolymers or mixed polymers of lactones, preferably with bifunctional addition products of lactones or lactone mixtures exhibiting end position hydroxyl groups, such as for example  $\epsilon$ - caprolactone,  $\beta$ - propiolactone,  $\gamma$ - butyrolactone and/or methyl-  $\epsilon$ - caprolactone with suitable bifunctional starter molecules, such as for example the previously mentioned low molecular bivalent alcohols serving as formulation components for the polyester polyols. The corresponding polymers of  $\epsilon$ - caprolactone are especially preferred. Low polyester dihydric alcohols or polyether dihydric alcohols can also be used as starters for the production of lactone polymers. In place of polymers from lactones, the corresponding, chemically equivalent condensation polymers of the hydroxycarboxylic acids corresponding to the lactones can also be used.

The polyether polyols, in particular the polyether dihydric alcohols, that can be added - possibly into the mixture with the polyester polyols - , can specifically be obtained by polymerization of ethylene oxide, propylene oxide, butylene oxide, tetrahydrofuran, styrene oxide, or of epichlorohydrin with itself/themselves, for example, in the presence of  $\text{BF}_3$  or by the addition of these compounds possibly into the mixture or possibly by sequential addition to the starter components having hydrogen atoms capable of reacting together, such as alcohols or amines, for example water, ethylene glycol, propylene glycol- (1,3) or -(1,2), 4,4'- dihydroxy-diphenyl propane, aniline.

As c) polyols with a molecular weight between 62 and 399 g/ mole, the following are suitable: for example, the corresponding dihydric and trihydric alcohols listed under b), suitable for the production of polyester polyols, as well as the alcohols that are higher than trifunctional, such as pentaerythritol or sorbitol.

In the case of the d) components that can possibly be added, we are dealing with at least bifunctional amine chain elongators or cross linking agents with a molar weight range of 32 to 500 g/ mole, preferably of 60 to 300 g/ mole, without tertiary amino groups. Examples of this are diamines such as ethylene diamine, hexamethylene diamine, piperazine, 2,5- dimethyl piperazine, 1- amino- 3 amino methyl- 3,5,5- trimethyl- cyclohexane (isophorone diamine, IPDA), 4,4- diamino- dicyclohexyl methane, 1,4- diamino- cyclohexane, 1,2- diamino- propane, hydrazine, hydrazine hydrate or triamine such as diethylene triamine. They can be added in moieties of 0 to 2.0 moles/ mole of b) component, in particular to elongate the chains of prepolymers containing isocyanate groups, prior to or, in particular in the case of triamines, after dispersion in water. The amino group containing chain elongators can be added in the block form, for example in the form of the corresponding ketimines (for example, compare to patent CA-PS 11 29 128), ketazines (compare to US patents 42 69 748 and 42 69 748) or amine salts (refer to US patent 42 92 226). Even oxazolidines, as they are used for example in the US patents 41 92 937 and 41 92 937, represent disguised diamines that can be used for the production of polyurethane dispersions, in accordance with the invention, for the purpose of elongating the chains of the isocyanate prepolymers. When using such disguised diamines, they are generally mixed together with the isocyanate prepolymers in the absence of water and this mixture is then subsequently mixed with the dispersion water or with part of the dispersion water so that the corresponding diamines are released by intermediary hydrolysis.

In the case of e) components to be possibly added, we are dealing with amino alcohols such as ethanolamine, isopropanolamine, methyl ethanolamine or amino ethoxy ethanol.

As f) formulation components, compounds are added which exhibit at least one, preferably two groups capable of reacting with isocyanates groups and in addition to that, which exhibit ionic groups or potential ionic groups that can be transformed into ionic groups by a simple neutralization reaction or by a quaternization reaction. By introducing the f) formulation components, the polyurethanes themselves become dispersible, that is, during the dispersion

process in the water, dispersing adjuvants (protective colloids or emulsifiers) are no longer required in this case. The introduction of cationic and anionic groups is achieved by the concurrent use of compounds exhibiting (potential) cationic groups with hydrogen atoms capable of reacting with isocyanate groups or by the concurrent use of compounds exhibiting (potential) anionic groups with hydrogen atoms capable of reacting with isocyanate groups. Belonging to this group of compounds, for example, are polyethers exhibiting tertiary nitrogen atoms preferably with two end position hydroxyl groups, as they are normally obtainable by alkoxylation of two amines exhibiting hydrogen atoms attached to amino nitrogen such as, for example, N- methyl amine, aniline or N,N'- dimethyl hydrazine. Such polyethers generally exhibit a molar weight ranging between 500 and 6,000 g/ mole. But preferably, the ionic groups are introduced by the concurrent use of relatively low molecular compounds with (potential) ionic groups and with groups capable of reacting to isocyanate groups. Examples for these are listed in the patents US 34 79 310 and 40 56 564 as well as in patent GB 14 55 554. Dihydroxy phosphonates can also be concurrently used as ionic formulation components such as, for example, the sodium salt of 2,3- dihydroxy propane phosphonic acid ethyl ester or the corresponding sodium salt of the non-esterified phosphonic acid.

Especially preferred (potential) ionic f) formulation components are N- alkyl dialkanolamines such as, for example, N- methyl diethanolamine, N-ethylene diethanolamine, diamino- sulfonates such as the sodium salt of N- (2- amino- ethyl)- 2 amino- ethane sulfonic acid, dihydroxy sulfonates, dihydroxy carboxylic acids such as dimethylol propionic acid, diamino- carboxylic acids or diamino- carboxylates such as lysine or the Na- salt of N- (2- amino- ethyl)-2- amino ethane carboxylic acid and diamines with at least one additional tertiary amino nitrogen atom such as, for example, N- methylbis- (3- amino- propyl)- amine.

Given the case, the transformation of the potential ionic groups initially integrated in the polyaddition product, or at least the partial transformation into ionic groups, occurs in the normal manner by neutralization of the potential anionic and cationic groups or by the quaternization of tertiary amino nitrogen atoms.

For the neutralization of potential anionic groups such as that, for example, of carboxyl groups, inorganic and/or organic bases are added such as sodium hydroxide, potassium hydroxide, potassium carbonate, sodium hydrogen carbonate, ammonia or primary, secondary and especially tertiary amines such as, for example, triethyl amine or dimethyl aminopropanol.

For the transformation of potential cationic groups such as that, for example, of the tertiary amine groups into the corresponding cations such as, for example, ammonia groups, inorganic and organic acids are suitable as neutralizing agents such as, for example, sodium salt, acetic acid, fumaric acid, maleic acid, lactic acid, tartaric acid, oxalic acid or phosphoric acid, or suitable as quaternization agents are, for example, methyl chloride, methyl iodide, dimethyl sulfate, benzyl chloride, chloroacetic acid ethyl ester or bromo- acetamide. Additionally suited neutralization and quaternization agents are described, for example, in the US patent 34 79 310, column 6.

This neutralization or quaternization of the potential ionic groups can be conducted prior to, during, but preferably after the isocyanate polyaddition reaction.

The quantities of f) formulation components in the case of potential ionic group containing components under consideration of the degree of neutralization or quaternization, must be properly selected such that the polyurethanes exhibit an ionic group content of 0.05 to 2 m equivalent/ g of polyurethane, preferably 0.07 to 1.0 and especially preferred of 0.1 to 0.7 m equivalent/ g of polyurethane.

In the case of the g) components to be possibly used concurrently, we are dealing preferably with monovalent polyether alcohols with a molar weight range of 500 to 10,000 g/ mole, preferably of 1,000 to 5,000 g/ mole. Monovalent polyether alcohols are obtainable by alkoxylation of monovalent starter molecules such as, for example, methanol, ethanol or n-butanol, whereby ethylene oxide or mixtures of ethylene oxide with other alkylene oxides, especially with propylene oxide, are used as alkoxyating agents. In the event of using alkylene oxide mixtures, they should however preferably contain at least 40 mole %, but especially preferred, at least 65 mole % of ethylene oxide.

By the use of the g) components, the polyethylene oxide segments present can thus possibly be integrated into the polyurethanes in the polyether chains arranged in the end positions or in the side positions and thus together with the ionic groups, they can influence the hydrophilic characteristics in the polyurethane.

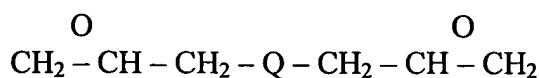
The compounds of the type mentioned, with the polyethylene oxide units present within the polyether chains arranged at the end and/or side positions, to the extent that they are used, can be added in such quantities that the polyethylene oxide units in the polyurethanes are present in the polyurethane dispersions at a rate of 0 to 10, preferably 0 to 5 weight % within the polyether chains arranged at the end and/or side positions. The total quantity of hydrophilic structural units (ionic groups and ethylene oxide units of the last mentioned type) must however always be selected such that the ability of the polyurethanes to disperse in water is always ensured.

Further examples of compounds that can be used for the production of the dispersions in accordance with the invention as components a) through e) are described, for example, in "High Polymers", vol. XVI, "Polyurethanes, Chemistry and Technology" by Saunders - Frisch, Interscience Publishers, New York, London, volume I, 1962, pages 32 through 42 and pages 44 through 54, and volume II, 1964, pages 5 through 6 and 198 through 199.

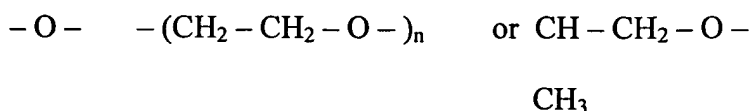
Coming under consideration as compounds with ethylenic unsaturated h) groups are, for example, esters of acrylic acid or of methacrylic acid with polyols, whereby at least one OH group of the polyol remains non-esterified. Especially suited are the hydroxy alkyl (meth) acrylates  $\text{HO}(\text{CH}_2)_n \text{OOC}(\text{R}^1) \text{C} = \text{CH}_2$  ( $n = 2$  to  $8$ ;  $\text{R}^2 = \text{H}, \text{CH}_3$ ) and their positional isomers, mono(meth)acrylic acid ester of polyether diols  $\text{HO}(\text{CHR}^2\text{CHR}^3\text{O})_m \text{OC}(\text{R}^1) \text{C} = \text{CH}_2$  ( $\text{R}^1 = \text{H}$ ,

CH<sub>3</sub>; R<sup>2</sup> = H, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>; m = 2 through 20), trimethylol propane mono- and di- (meth)acrylate, penta- erythritol- di- and tri- (meth)acrylate or reaction products of epoxide compounds with (meth) acrylic acids such as they are named, for example, in the patent US-A- 3 57 221. Especially suitable for coatings with great hardness are the adducts of (meth)- acrylic acids with compounds having the general formula:

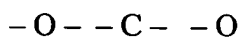
[refer to original formulas]



in which Q stands for e.g.,



with  $n = 1 - 10$ ,  $-O-(CH_2)_mO-$  with  $m$  signifying  $= 1$  to  $8$  or  $Q$  stands for a group



whereby this group can be derived, for example, from 4,4' - dihydroxy diphenyl methane, bisphenol A, bisphenol K or from atom substituted or hydrogenated derivatives of these compounds.

Adducts of (meth)- acrylic acid to epoxidized diolefins can also be used such as, for example, 3,4- epoxy cyclohexyl methyl- 3',4' - epoxy cyclohexane carboxylate.

Especially preferred is the adduct of acrylic acid to the bisglycidyl ether of bisphenol A.

The production of the A) polyurethane can be conducted according to conventional methods as they are described, for example, in the German patent DE-A- 34 37 918.

Preferably, a first stage is initially produced from components a), b), h), possibly from c), e), g), h) and f), provided f) does not contain any amino groups, with the isocyanates still in end position, and in an inert water miscible solvent such as acetone, tetrahydrofuran, methyl ethyl ketone or N- methyl pyrrolidone. The reaction temperature preferably lies between 50 and 100°C.

To accelerate the reaction of the diisocyanates, the conventional and known catalysts, such as dibutyl tin dilaurate, tin- II- octoate or 1,4- diazabicyclo- (2,2,2)- octane can be used in conjunction.

In order to avoid an undesirable premature polymerization of the unsaturated groups,



polymerization inhibitors are advantageously added as early as the production of the polyurethane. Suitable examples for this are quinones, phenothiazines, phenols or phenol derivatives such as p- benzoquinone, hydroquinone, p- methoxy phenol among other compounds and such as described in the "Encyclopedia of Polymer Science and Technology", vol. 7, 1967, p. 644 - 664, editors: Mark, Gaylord and Bikales, Interscience Publishers, Wiley + Sons, New York - London - Sidney.

The polyurethane obtained in this manner can possibly be further transformed, after (further) dilution with solvents of the type mentioned above, preferably with solvents having low boiling points below 100°C, at a temperature ranging between 20° and 80°C, with amino functional products of components f) and possibly of components d).

The transformation of potential salt groups such as, for example, carboxyl groups or tertiary amino groups, which are introduced into the polyurethane via the f) component, into the corresponding ions is achieved by neutralization with bases or with acids or by quaternization of the tertiary amino groups prior to or after dispersing the solution in water.

After the solution has been dispersed in the water, the organic solvent is distilled off.

The weight percentage of the water in the dispersion is generally measured such that the aqueous polyurethane dispersions are obtained as having a solid content of 10 to 60 weight %, preferably of 20 to 50 weight %.

In addition to containing component A), the irradiation curable, aqueous binding agent dispersion in accordance with the invention contains 5 to 95 weight %, relative to the total quantity of (A), (B) and (C), of a prepolymer or prepolymer mixture (B), dispersed in water, with a content of 0.1 to 1.0 mole of polymerizable ethylenic unsaturated groups per 100 g. of prepolymer or prepolymer mixture and with a molecular weight of 300 to 10,000 g/ mole, whereby the K-value (measured at 25°C in dimethyl formamide) is less than 40.

The prepolymer or prepolymer mixture preferably contains 0.1 to 0.5 mole of polymerizable ethylenic unsaturated groups.

The molecular weight preferably amounts to 300 through 1,000 g/ mole. The K-value is preferably less than 30, especially preferred less than 20.

As a rule, the prepolymer or prepolymer mixture is as such liquid at 20°C and at normal pressure.

When using a prepolymer mixture, prepolymers can be added that are solid at 20°C and at normal pressure, so long as the prepolymer mixture is liquid.

When using liquid and solid prepolymers, it is not absolutely necessary to initially produce a

liquid prepolymer mixture. The individual prepolymers can be separately dispersed in the water. What matters is that the prepolymers yield a liquid phase in the mixture and that they are mobile in contrast to the non-flowing polyurethane particles (A). This contributes considerably toward the formation of a film and the development of a better composite.

In the case of prepolymers, we can be dealing with polyesters, polyethers, polyepoxides, polyurethanes or radically polymerized polymers or copolymers that contain polymerizable double carbon bonds by reaction with compounds such as acrylic acid or methacrylic acid.

The following prepolymers are preferred:

1. In the case of the polyesters, we are preferably dealing with polyesters, with an acid index of 10 at the most, that can be produced according to conventional processes from (cyclo) aliphatic  $C_5$  through  $C_{12}$  or  $C_2$  through  $C_{12}$  and/or from aromatic  $C_5$  -  $C_{14}$ -dicarboxylic acids such as succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, cyclohexane dicarboxylic acid, phthalic acid, isophthalic acid, terephthalic acid, maleic acid, fumaric acid, itaconic acid or derivatives thereof, and preferably from 2- to 5- valent  $C_2$  -  $C_{10}$  alcohols such as ethylene glycol, polyethylene glycols, propylene glycol, polypropylene glycol, butanediol, hexanediol, neopentyl glycol, hydroxy pivalic acid neopentyl glycol ester, trimethylol propane, glycerin, pentaerythritol as well as  $\alpha$ ,  $\beta$ - ethylenic unsaturated monocarboxylic acids such as, for example, acrylic acid, methacrylic acid, crotonic acid, cinnamic acid, and/or dicarboxylic acid semi-ester of mono-alcohols such as maleic, fumaric and itaconic acid semi-ester with  $C_1$  -  $C_4$  mono-alcohols, whereby acrylic acid and methacrylic acid are preferred.
2. In the case of the polyethers, we are preferably dealing with aliphatic polyethers that are obtained by reacting bivalent or polyvalent, specifically bivalent or trivalent  $C_2$  -  $C_{10}$  alcohols, with epoxides such as, for example, ethylene oxide or propylene oxide and ethylenic unsaturated alcohols such as, for example, allyl alcohol, methallyl alcohol, crotonyl alcohol, (meth-) acrylic acid esters containing hydroxy groups or preferably ethylenic unsaturated monocarboxylic acids such as, for example, acrylic acid or methacrylic acid.
3. In the case of the polyepoxides we are preferably dealing with polyepoxides with an average of 2 to 4, in particular 2 epoxide groups per molecules, for example, polyglycidyl ether of polyvalent alcohols, as they are also enumerated under 1), polyglycidyl ether of polyvalent phenols such as bisphenol A, novolacs, glycidyl ester of polyvalent carboxylic acids, as they are also enumerated under 1), other glycidyl compounds, for example, triglycidyl isocyanurate, that are reacted with ethylenic unsaturated carboxylic acids as they are also enumerated under 1), in particular acrylic acid and methacrylic acid.
4. In the case of polyurethanes, we are preferably dealing with a polyurethane possibly containing carbamide groups which can be produced from  $C_2$  -  $C_{10}$  aliphatic and/or  $C_5$  -  $C_{20}$  aromatic polyisocyanates, preferably from diisocyanates such as for example tetramethylene diisocyanate, hexamethylene diisocyanate, isophorone diisocyanate, diphenyl methane diisocyanate, toluylene diisocyanate, naphthylene diisocyanate, 4,4'-

diphenyl ether diisocyanate, possibly dimers or trimers obtained therefrom, for example their isocyanurates, biurets, allophanates as well as transformation products thereof, and from hydrogen active compounds such as, for example, polyvalent alcohols, that are enumerated under 1), from polyfunctional amines and/or amino alcohols, as well as from hydroxyl group containing  $C_1 - C_{12}$ -alkyl (meth) acrylates such as hydroxy ethyl (meth)-acrylate hydroxy propyl (meth-) acrylate and/or butanediol mono (meth-) acrylate. The sum of the gram equivalents of the hydroxyl groups and amino groups reacting to the isocyanate amounts to preferably 0.95 to 1.05 relative to 1 gram equivalent of isocyanate.

5. In the case of radically polymerized polymers or co-polymers, we are preferably dealing with copolymers of styrene and/or of acrylic esters such as, for example,  $C_1 - C_{12}$ -alkyl (meth-) acrylates, with low quantities of functionalized monomers such as, for example,  $C_1 - C_8$ -hydroxy alkyl (meth-) acrylates or glycidyl (meth) acrylate, (meth) acrylic acid, maleic acid anhydride, isocyanato ethyl acrylate, which are reacted with ethylenic unsaturated compounds as they are enumerated, for example, under 1), or as previously mentioned, but in particular with acrylic acids and methacrylic acids, and thus exhibit a content in polymerizable double bond carbon atoms.

Especially preferred are polyesters, polyethers and polyepoxides. The prepolymers can also be amine modified, for example, by addition of primary and secondary amines to double bonds (Michael addition). The (B) component can initially be present in dissolved form in an organic solvent or in a solvent mixture such as, for example, in the solvent used during the production of the (B) component. Suitable organic solvents are, for example, tetrahydrofuran, dioxane, acetone, methyl ethyl ketone, propanols, butanols, ethyl acetate, butyl acetate, methylene chloride, xylenes or toluenes; preferred are methyl ethyl ketone, tetrahydrofuran, isopropanol and isobutanol. The (B) component solution is then dispersed in water and the organic solvents are distilled off. Component (B) can also be directly dispersed in water.

In general, the solid matter content of such aqueous dispersions of component (B) amounts to 20 through 80 weight %.

Component (B) can be self-dispersing so that no dispersing adjuvants are required (protective colloid or emulsifier). Preferably, it is not self-dispersing and it is dispersed with the help of a protective colloid. Therefore, a protective colloid is added to the water prior to the dispersion of component (B) or prior to the organic dissolution of component (B).

In this case, the protective colloid is generally added to (B) in quantities of 0.1 to 30, preferably 3 to 12 weight % relative to (B). Here, we are dealing preferably with water soluble, high molecular organic compounds with polar groups such as, for example, polyvinyl pyrrolidone, copolymers of vinyl propionate or vinyl acetate and vinyl pyrrolidone, with partially saponified copolymers of acrylic ester and acrylic nitrile, polyvinyl alcohols with various residual acetate contents, cellulose ether, gelatin or mixtures of these substances. Especially preferred protective colloids are polyvinyl alcohols with a residual acetate content of under 35, in particular of 5 to 30 mole % and/or a vinyl pyrrolidone-/ vinyl propionate copolymer with a vinyl

ester content of under 35, in particular of 5 to 30 weight %.

Furthermore, non-ionic emulsifiers can be used and in special cases, ionic emulsifiers as well. Preferred emulsifiers are longer chain alcohols or phenols with various degrees of ethoxylation and/or propoxylation (adducts of 4 to 50 moles of ethylene oxide and/or propylene oxide). Especially advantageous are combinations of the above mentioned protective colloids mixed with such emulsifiers because finer particle dispersions can be obtained by using them.

The binding agent dispersion in accordance with the invention contains as (C) component 0 to 30 weight %, preferably 0.1 to 10 weight %, especially preferred 0.5 to 10 weight % relative to the total quantity of (A), (B) and (C) of a previously mentioned protective colloid.

For the production of the irradiation curable binding agent dispersions in accordance with the invention, the aqueous dispersions of components (A) and (B) can be mixed together.

Preferably, an aqueous dispersion of a self-dispersing polyurethane (A) is mixed with the aqueous dispersion of a prepolymer (B) which is dispersed with the help of a protective colloid.

The binding agent dispersion in accordance with the invention preferably contains 19.9 to 80 weight %, especially preferred 40 to 79.5 weight %, relative to the total quantity of (A), (B) and (C) of the component (A).

The weight percentage of component (B) accordingly amounts to a preferable 19.9 through 80 weight %, especially preferred is 20 to 59.5 weight % relative to the total quantity of (A), (B) and (C).

The solid matter content of the binding agent dispersion in accordance with the invention can accordingly be adjusted to obtain the desired viscosity. Generally, the solid matter content lies between 20 and 80, in particular between 20 and 70 weight %.

The dispersions in accordance with the invention can contain additional ingredients such as, for example, pigments, dyes, filling agents and other adjuvant substances that are standard in the coatings technology.

For curing by irradiation with UV- light, photo initiators are added to the dispersions.

Coming under consideration as photo initiators are, for example, benzophenone, alkyl benzophenone, halogen methylated benzophenones, Michler's ketone, anthrone and halogenated benzophenones. Furthermore, benzoin and its derivatives are suitable. Equally effective photo initiators are anthraquinone and many of its derivatives such as, for example,  $\beta$ - methyl anthraquinone, tertiary butyl anthraquinone and anthraquinone carboxylic acid ester and acyl phosphine oxide, for example, Lucirin® TPO. The photo initiators can also be attached to the polymer structure, for example, by co-polymerization of photo initiators functionalized with

methacrylate groups.

Depending on the application purpose of the masses in accordance with the invention, the photo initiators that are used in quantities of between 0.1 and 20 weight %, preferably from 0.1 to 5 weight %, relative to the polymerizable components, can either be used as individual substances or, based on the common advantageous effects of synergy, also in combination with one another.

Advantageous additives that can contribute to further increasing reactivity are found in certain tertiary amines such as, for example, triethylamine and triethanolamine. They can also be used in quantities of up to 5 weight % relative to the polymerizable components.

In concluding, it is noteworthy to mention that the dispersions in accordance with the invention can also be thermally cross linked. For this, it is necessary to add initiators that form radicals at the more elevated temperatures. For example, dibenzoyl peroxide, cumene hydroperoxide or azodiisobutyric acid dinitrile can be used. Further examples of suitable initiators are described in the "Polymer Handbook", 2<sup>nd</sup> edition, Wiley & Sons, New York.

The dispersions in accordance with the invention can be used for the production of coatings.

They can be applied for example by spraying, casting, pressure casting/printing or by doctor blade on substrates such as metal, plastics, glass, wood, paper, cardboard, leather or textiles.

During irradiation curing, the protective layers are generally preheated for up to 30 minutes at temperatures of up to 100°C and subsequently exposed to ultraviolet light or high energy electron beams for a short period. To this end, conventional ultraviolet or electron beam sources are used for curing the protective layers. In order to maintain the shortest possible preliminary heating periods, relatively low molecular prepolymers are preferred for reasons of viscosity.

In the case of porous substrates such as, for example, leather, paper and wood, just very short preliminary heating periods are required because the major part of the water is absorbed by the substrate; sometimes, preliminary heating can be skipped altogether.

The coatings simultaneously exhibit very good elastic properties while maintaining great hardness.

Even the adhesion of the coatings and the resistance to chemicals are very good.

#### Example 1

Polyurethane dispersion a<sub>1</sub>)

200 weight parts of a polyester of adipic acid, isophthalic acid (molar ratio of 1 : 1) and 1,6 hexanediol (OH = number 112), 43 weight parts of 1,4- butanediol, 60 weight parts of bisphenol-A- diglycid ether acrylate (adduct of 2 moles of acrylic acid to bisphenol- A- diglycid ether), 53 parts of dimethylol propionic acid and 100 parts of N- methyl- pyrrolidone were dehydrated in a vacuum at 70°C and reacted with 322 weight parts of isophorone diisocyanate at 90°C to the point of yielding an NCO- content of 2.75 weight %. After dilution with 800 weight parts of acetone, 32 weight parts of dimethyl ethanolamine were added and the solution was dispersed in 1,500 weight parts of water within 10 minutes. After 5 minutes, 21 parts of isophorone diamine and 9 weight parts of diethylene triamine were added in 140 weight parts of water. The acetone was distilled off. A part of the dispersion was dried at room temperature, upon which a film developed which was insoluble in dimethyl formamide.

#### Prepolymer dispersion b)

18 weight % of bisphenol- A- diglycid ether acrylate  
 27 weight % of an alkoxyated trimethylol propane acrylate (molar weight: 500 g/ mole; 100 Pa. - s at 23°C, Laromer® LR8748 BASF AG)  
 5 weight % of polymer of N- vinyl pyrrolidone and vinyl propionate with a weight ratio of 66 : 34.  
 50 weight % of water.

117 g. of polyurethane dispersion were mixed with 30 g. of prepolymer dispersions, 2 g. of a photo initiator, benzophenone/ 1- hydroxy- cyclo- hexyl- phenyl- ketone (Irgacure® 500, by Ciba - Geigy AG) were added and the solid matter content of the dispersion was adjusted to 30 weight % with water. The weight ratio of the polyurethane/ prepolymer amounted to 70 : 30.

The dispersion was applied to semi-mat art paper (KD paper) and dried at 40°C for 20 minutes and transported past the high pressure mercury vapor lamp (120 Watts/ cm) on the conveyor below at a distance of 10 cm from it. An 8 µm thick layer could be cured at a conveyor speed greater than 78 m/min and hardened against fingernail scratching.

A 40 µm layer on glass had a pendulum damping value (DIN 53 157) of 115 s. after twice being exposed to light at a conveyor speed of 10 m/ min. The Olsen cupping index (DIN 53 156) of a 20 µm thick layer, hardened twice at a conveyor speed of 10 m/ min, on bonderizing tin 132 amounted to 9.8 mm. The adhesion of this layer with or without cross cutting, the resistance to chemicals (DIN 68 860 B), surface smoothness and grindability were very good.

#### Example 2

##### Polyurethane dispersion a<sub>2</sub>)

200 weight parts of a polyester of adipic acid, isophthalic acid (molar ratio of 1 : 1) and 1,6 hexanediol (OH number 112), 80 weight parts of 1,4- butanediol, 60 weight parts of bisphenol-A- diglycid ether acrylate, 54 weight parts of dimethylol propionic acid, 0.1 weight parts of p-methoxy phenol and 100 weight parts of N- methyl- pyrrolidone were dehydrated in a vacuum at 70°C and were reacted with 411 weight parts of isophorone diisocyanate at 90°C to the point of yielding an NCO- content of 2.34 weight %. After dilution with 800 weight parts of acetone, 28 weight parts of dimethyl ethanolamine were added and the solution was dispersed in 1,000 weight parts of water within 10 minutes. After 5 minutes, 21 weight parts of isophorone diamine and 9 weight parts of diethylene triamine were added in 40 weight parts of water. The acetone was distilled off. The polyurethane was insoluble in dimethyl formamide.

In analogy to example 1, a dispersion was produced from a<sub>2</sub> and b) with a solid matter content of 30 weight % in which the weight ratio of polyurethane to prepolymer was 70 : 30.

Resistance to scratching by fingernail was obtained at 45 m/ min. The pendulum damping value amounted to 105 s, the Olsen cupping index was over 10 mm. Adhesion, resistance to chemicals and surface smoothness were very good.

#### Comparative example

The solid matter content of the prepolymer dispersion b) was set to 30 weight %. Resistance to scratching by fingernail was attained at 10 m/ min. The pendulum damping value amounted to 130 s and the Olsen cupping index was only 3 mm. The resistance to chemicals was very good, however adhesion was only satisfactory.

#### Patent claims

1. Irradiation curable, aqueous binding agent dispersions containing  
 (A) 5 to 95 weight %, relative to the total quantity of components (A), (B) and (C), of a polyurethane dispersed in water, which has a K-value greater than 40 (measured in dimethyl formamide) or which is not soluble in dimethyl formamide and which exhibits a content of polymerizable ethylenic unsaturated groups of a maximum of 0.2 moles per 100 g of polyurethane, and  
 (B) 5 to 95 weight %, relative to the total quantity of components (A), (B) and (C), of a prepolymer or of a prepolymer mixture dispersed in water with a content of 0.1 to 1.0 mole of polymerizable ethylenic unsaturated groups per 100 g of prepolymer or of prepolymer mixture and with a molecular weight of 300 to 10,000, whereby the K-value (measured in dimethyl formamide) is smaller than 40, and  
 (C) 0 to 30 weight %, relative to the total quantity of the components (A), (B) and (C), of a protective colloid.
2. Process for the production of binding agent dispersions in accordance with claim 1, thus

characterized that an aqueous dispersion of a self dispersing polyurethane (A) is mixed with the aqueous dispersion of a prepolymer (B) which is present in dispersed form with the help of a protective colloid.

3. Application of aqueous binding agent dispersions in accordance with claim 1 for the production of coatings that are cured by irradiation with high energy beams.
4. Coated substrates obtained by the use of a binding agent dispersion in accordance with claim 1.